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COMPLETE SPECIFICATION.

Compositions for Rendering Textile Materials Resistant to Creasing.

We, FARBWERKE HOECHST A.G., vormals Meister Lucius & Brüning, a company recognised by German law, of 6230 Frankfurt (M)-Hoechst, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

Fabrics of natural or regenerated cellulose fibres, either alone or in admixture with totally synthetic fibres are not sufficiently stable in shape, i.e. they do not completely recover after being subjected to a strong mechanical strain, and they do not return to their original shape. In view of this, textile materials of said kind have for a long time been subjected to a crease-proof finish, in order to enable the fabric to retain is original shape after normal wear.

Many processes are known for rendering textile materials crease-proof. For the purpose in question, formaldehyde precondensates of urea, thiourea or melamine hardenable by means of acid are preferably used. At the present time hardenable reactive resins are used, especially for the finishing of cotton fabrics. The most important types of these are for instance: dimethylol-ethylene-urea, dimethylol-propylene-urea, dimethylol-hydroxy-ethyl-triazinone and dimethylol-dihydroxy-ethylene-urea. Moreover, condensation compounds free from nitrogen have also been used to obtain a crease-proof finish, for instance polyfunctional formals, polyfunctional epoxide resins for example, glycol-diglycidyl ethers and glycerine-diglycidyl ethers which are usually condensed under acid conditions by means of zinc-fluoborate. The resistance to creasing attained with the above-mentioned compounds is still unsatisfactory as regards the crease-recovery in a wet as well as in a dry state.

It is also known that bi- or trifunctional ethylene-imine compounds, for example, tris-aziridinyl-(1)-phosphine oxide, tris-2-methyl-aziridinyl-(1)-phosphine oxide and 1, 6-di-(N-ethylene-ureido)-hexane, which may be condensed under acid conditions with zinc-fluoborate, when applied to fabrics of natural or regenerated cellulose fibres result in considerably improved crease-recovery in the wet and dry state.

The present invention is based on the observation that the crease recovery attained by the known processes imparting a high quality finish, for instance by using the above-mentioned compounds, can be greatly improved by using ethylene-propylene-copolymer dispersions which have been subjected to graft polymerisation. This applies to the crease-proof finish of natural and regenerated cellulose fibres, as well as to these fibres in admixture with fully synthetic fibres, in so far as the proportion of synthetic fibre present is not sufficient to cause resistance to creasing.

The invention thus provides a process for improving the resistance of textile materials to creasing, said materials consisting of a) natural or regenerated cellulose fibres or b) natural or regenerated cellulose fibres in admixture with a proportion of synthetic fibres that is insufficient to impart to the material resistance to creasing, which comprises treating the textile material in a finishing

bath with an aqueous dispersion of an aminoplast resin, a polyfunctional formal resin, a polyfunctional expoxide resin or a bi- or trifunctional ethylene-imine compound together with an agent having an acid reaction and fixing said crease-proofing agent on the fibres by a thermosetting process as hereinafter described, the improvement with regard to crease resistance being effected by simultaneously adding to the finishing bath an aqueous dispersion of an ethylene-propylene copolymer or an aqueous dispersion of a terpolymer comprising units of ethylene, propylene and a third monomer, the copolymer or terpolymer having been subjected to graft polymerisation with a monomer containing a functional group, which group renders the grafted polymer cross-linkable.

The invention also provides compositions for rendering cellulosic textile materials resistant to creasing comprising an aqueous dispersion of an aminoplast resin, a polyfunctional formal resin, a polyfunctional epoxide resin or a bi- or trifunctional ethylene-imine compound together with an agent having an acid reaction, which composition further contains an aqueous dispersion of an ethylene-propylene copolymer or an aqueous dispersion of a terpolymer comprising units of ethylene, propylene and a third monomer, the copolymer or terpolymer having been subjected to graft polymerisation with a monomer containing a functional group, which group renders the grafted polymer cross-linkable.

The graft polymerisation is carried out by using monomers containing suitable functional groups, which groups render the grafted polymers cross-linkable and are preferably the $-NH_2$ or $-CO-NH_2$ groups. Examples of appropriate compounds are acrylamide and acrylic acid β-aminoethyl ester.

The amount of the above-mentioned monomers grafted on to the copolymer or terpolymer may be within the range of 1 to 50% by weight, preferably 10 to 30% calculated on the copolymer or terpolymer. The preparation of polymer dispersions suitable for being grafted and the grafting itself can be carried out by a process in which highly amorphous saturated copolymers of ethylene with α-olefines are reacted with acrylamide and its derivatives substituted on the nitrogen atom by alkyl groups, in the presence of free radical initiators. Another process for preparing aqueous, stable dispersions of co-polymers, (especially those obtained by low-pressure methods) of α-olefines with solids contents of more than 40%, by emulsification in water of a solution of the polymer in an organic solvent, in the presence of,

a) a known, non-ionic and/or ionic emulsifier and

b) a high-molecular ionic compound, with subsequent removal of the organic solvent by distillation and concentration of the dispersion by creaming, is advantageously carried out according to the procedure described in Specification No. 993,664. Advantageously, as the substance mentioned under b) above, there may be used a polymer containing water-soluble sulphate or sulphonate groups obtained by polymerisation of an unsaturated monomer with a carbon-carbon double linkage and, if necessary, modifying the formed polymer, the sulphate or sulphonate groups being present as alkali metal and/or ammonium salts. Concentrated aqueous dispersions of olefine copolymers with positively charged particles can be obtained according to the procedure described in Specification No. 1,001,948, if they contain, as emulsifier, salts of weak acids with quaternary ammonium bases in a concentration within the range of 4 to 20% calculated on the weight of the polymer.

Instead of the ethylene-propylene-copolymer dispersions, there may be used for the grafting process dispersions of terpolymers comprising ethylene and propylene units, for instance, ethylene-propylene-biscyclopentadiene-terpolymer. Products of this type possess the advantage that they impart to the textile materials treated therewith greater dirt-resisting properties than in the case of grafted ethylene-propylene-copolymer dispersions.

When the above-mentioned copolymer or terpolymer dispersions have been grafted with acrylamide, it is advantageous to react them with formaldehyde prior to using them for textile finishing, 1—2 mols of formaldehyde being preferably used for mol of combined acrylamide.

The aqueous dispersions of the grafted olefine copolymers or terpolymers are added to the finishing baths and are applied simultaneously with the agents for imparting crease-proof finish, and the agents having an acid reaction. They can be applied by dipping, spraying, painting, padding and the like. Preferably, a padding machine is used. After the application of the finishing substance, any excess is removed by squeezing the material, after which it is subjected to a thermosetting process. This consists of an intermediate drying process which is carried out at a temperature not greater than 120°C, preferably in the temperature range of 80 to 120°C, and more preferably 90 to 110°C. After the preliminary drying, the temperature is adjusted to within the range of 120 to 180°C, preferably 140 to 160°C and the polycondensation of the aminoplast or other precondensate resin referred to above takes place. In general, the period during which condensation takes place is reduced by using a higher temperature.

The use of the aqueous dispersions of grafted copolymers or terpolymers according to the invention considerably improves the crease angle of the fabric in the wet and in the dry state. Moreover, the fabrics finished according to the process of the present invention have a fully soft and supple handle. In order to improve the feel of the material, plasticizers or sizing agents may be added to the textile-treating compositions if desired.

The following Examples illustrate the invention:—

Example 1

a) A bleached and mercerised cotton poplin for shirts, having a weight of about 125 grams/sq.m. was treated on a padding machine with an aqueous finishing bath containing, per litre, 70 grams of dimethylol-ethylene-urea, 13.5 grams of magnesium chloride and 30 grams of an aqueous dispersion containing 25% by weight of an ethylene-propylene copolymer having a propylene content of 48 mol per cent grafted with 25% by weight of acrylamide, calculated on the copolymer. Moreover, the graft polymer had been reacted with 2 mols of formaldehyde for each mol of combined acrylamide. The fabric was then squeezed until it showed an increase in weight of about 75%. After drying on a nozzle-type stenter at 90°C, the resin was by condensed for 5 minutes at 150°C.

The addition of the aqueous polyolefine dispersion to the above-mentioned treating composition considerably improves the resistance to creasing of the fabric in the wet and dry state, and the effect does not deteriorate after repeated washing.

The following values were ascertained:

1) Without addition of the polyolefine dispersion
   a) crease angle (dry) ... ... 219° (measured according to German Industrial Standards 5389)
   b) crease angle (wet) ... ... 226° (determined according to the directions given by Tootal Broadhurst in Specification No. 727,889). The sum of crease angles was determined in warp and weft direction.
2) with addition of 30 grams per litre of polyolefine dispersion
   a) crease angle (dry) ... ... 265°
   b) crease angle (wet) ... ... 247°

It is surprising that although the resistance to creasing of the fabrics considerably increases, the loss in tensile strength is no greater than that obtained when only dimethylol-ethylene urea is used. The addition of the polyolefine dispersion also imparts to the fabric a fully soft and supple handle.

b) Instead of the above-described polyolefine dispersion, there was used an equal amount of an aqueous dispersion containing 25% by weight of an ethylene-propylene-biscyclo-pentadiene-terpolymer containing 38 mol per cent of propylene and 6 mol per cent of biscyclopentadiene, likewise grafted with 25% by weight of acrylamide calculated on the terpolymer, and likewise reacted with 2 mols of formaldehyde per mol of acrylamide. Processing was carried out as described above, and an excellently crease-proof cotton fabric was obtained showing considerably improved values as regards wet and dry crease angle, i.e.

dry ... ... 287°
wet ... ... 260°

It was likewise found in this case that in spite of the improved resistance to creasing, the tensile strength is only slightly modified in comparison with that of a fabric finished only with dimethylol-ethylene-urea. The fabric thus obtained was especially full and supple to handle. Moreover, it should be emphasized that the fabric showed good resistance to dirt.

Example 2

a) A mercerized, bleached cotton poplin fabric dyed with a sulphuric acid ester of a leuco vat dyestuff and suitable as dress material, which had a weight of 120 grams/sq. m. was treated on a padding machine by means of an aqueous finishing bath containing, per litre, 75 grams of dimethylol-dihydroxy-ethylene urea, 15 grams of magnesium chloride, 50 grams of ethylene-propylene-biscyclo - pentadiene - terpolymer dispersion grafted with acrylamide and formalized as described in example 1b) and 5 grams of octadecyl-ethylene-urea. The impregnation was carried out at room temperature. The fabric was squeezed until it possessed an increase in weight of about 70%. After a preliminary drying at 120°C, the condensation of the urea precondensate was carried out at 150°C for 5 minutes.

A cotton fabric excellently crease-proof in the dry and wet state was obtained, which also showed a very good resistance to chlorine. The effects were unchanged after washing at the boil.

Measurements of the crease angles when using dimethylol - dihydroxy - ethylene - urea and magnesium chloride alone gave the following values:

dry ... ... 216°
wet ... ... 221°

After adding the polyolefine dispersion, the crease recovery was increased to

281° ... ... (dry)
256° ... ... (wet).

The tensile strength and the resistance to rubbing were only slightly affected by the additional use of the polyolefine dispersion.

b) When the bath mentioned under a) was replaced by a bath of the following composition

85 grams of dimethylol-propylene-urea,
20 grams of magnesium chloride,
50 grams of the dispersion mentioned under 1a) of an ethylene-propylene-copolymer grafted with acrylamide, furthermore containing per 1 mol of acrylamide 2 mols of reacted formaldehyde
5 grams of octadecyl-ethylene-urea

and operating as described under 2a), the resistance to creasing of the cotton fabric in the dry and wet state was likewise considerably improved. After several washes at the boil, the fabric did not show any chlorine retention.

c) A fabric similarly provided with a very good crease-proof finish, and showing a fully soft and smooth handle, was obtained by using a bath containing, per litre, 35 grams of the di-methyl ether of di-methylol-urea, 35 grams of the trimethyl ether of hexamethylolmelamine, 30 grams of the dispersion described in example 1b and 15 grams of magnesium chloride. The fabric was initially dried at 100°C, and the condensation of the precondensate was subsequently carried out for 5 minutes at 150°C.

Example 3

A stable fibre muslin fabric printed with reactive dyestuffs was impregnated on a padding machine by means of an aqueous finishing bath of the following composition:

Per litre of bath:
75 grams of dimethylol-urea,
50 grams of the aqueous dispersion mentioned in example 1b),
5 grams of ammonium chloride,
5 grams of octadecyl-ethylene-urea.

After the fabric had been impregnated, it was initially dried at 80°C, and the hardening was carried out at 145°C.

In the dry state, the finished product showed a crease angle of 270°, whereas this angle was 242° when the aqueous dispersion was not added to the finishing bath. After finishing according to the process of the invention, the stable fibre fabric showed a fully soft and wool-like handle. The crease-proof effect was very resistant to washing.

Example 4

A mercerized and dyed twill cotton fabric weighing 125 grams/sq.m. was impregnated on a padding machine by means of an aqueous finishing bath containing, per litre,

130 grams of tris-aziridinyl-(1)-phosphine-oxide,
13 grams of an aqueous solution of zinc fluoborate (40% concentration) and
45 grams of the dispersion mentioned in example 1b).

After a preliminary drying at 120°C, the fabric was heated at 150°C in order to condense the resin precondensate. An excellently crease-proof product was obtained.

When operating as described above, but treating the finished material after the hardening step with a solution containing 5 grams of octadecyl-ethylene-urea per litre, and drying it at 120°C in the stenter, the resistance to creasing was increased by about 5 to 8%, due to the after-treatment by means of a plasticizer, i.e. octadecyl-ethylene-urea.

Example 5

A bleached and mercerized cotton poplin suitable for shirts and having a weight of 125 grams/sq.m. was impregnated at 25°C on a padding machine, with an aqueous finishing bath containing, per litre, 75 grams of glycol-diglycidyl ether, 15 grams of an aqueous solution of zinc fluoborate (40% concentration) and 30 grams of the dispersion described in Example 1a). After impregnation, the fabric was initially dried at 100°C, and then heated for 5 minutes to 150°C, in order to harden the resin precondensate. The dispersion of the grafted ethylene-propylene-copolymer, considerably increased the crease recovery of the material finished by means of glycol-diglycidyl-ether.

WHAT WE CLAIM IS:—

1. A process for improving the resistance of textile materials to creasing, said materials consisting of a) natural or regenerated cellulose fibres or b) natural or regenerated cellulose fibres in admixture with a proportion of synthetic fibres that is insufficient to impart to the material resistance to creasing, which comprises treating the textile material in a finishing bath with an aqueous dispersion of an aminoplast resin, a polyfunctional formal resin, a polyfunctional epoxide resin or a bi- or trifunctional ethylene-imine compound together with an agent having an acid reaction and fixing said crease-proofing agent on the fibres by a thermosetting process as hereinbefore described, the improvement with regard to crease resistance being effected by simultaneously adding to the finishing bath an aqueous dispersion of an ethylene-propylene copolymer or an aqueous dispersion of a terpolymer comprising units of ethylene, propylene and a third monomer, the copolymer or terpolymer having been subjected to graft polymerisation with a

monomer containing a functional group, which group renders the grafted polymer cross-linkable.

2. A process as claimed in Claim 1, wherein the monomer used for the graft polymerisation contains an $—NH_2$ or a $—CO—NH_2$ group.

3. A process as claimed in Claim 2, wherein the monomer is acrylamide or acrylic acid β-amino-ethyl ester.

4. A process as claimed in Claim 3, wherein acrylamide is used, and 1—2 mols of formaldehyde are reacted with the graft polymer dispersion per mol of combined acrylamide present in the graft polymer before applying the dispersion to the textile material.

5. A process as claimed in any one of Claims 1—4, wherein the amount of monomer grafted on to the copolymer or terpolymer is within the range from 1 to 50% by weight calculated on the copolymer or terpolymer.

6. A process as claimed in Claim 5, wherein 10 to 30% by weight of monomer is used.

7. A process as claimed in any one of Claims 1—6, wherein the terpolymer is ethylene - propylene - biscyclopentadiene - terpolymer.

8. A process according to Claim 1, conducted substantially as described in any one of the Examples herein.

9. Compositions for rendering cellulosic textile materials resistant to creasing comprising an aqueous dispersion of an aminoplast resin, a polyfunctional formal resin, a polyfunctional epoxide resin or a bi- or trifunctional ethylene-imine compound together with an agent having an acid reaction, which composition further contains an aqueous dispersion of an ethylene-propylene copolymer or an aqueous dispersion of a terpolymer comprising units of ethylene, propylene and a third monomer, the copolymer or terpolymer having been subjected to graft polymerisation with a monomer containing a functional group, which group renders the grafted polymer cross-linkable.

10. Compositions as claimed in Claim 9, wherein the terpolymer is an ethylene-propylene-biscyclopentadiene terpolymer.

11. Compositions as claimed in Claim 9 or 10, wherein the grafting monomer is acrylamide or acrylic acid β-amino-ethyl ester.

12. Compositions as claimed in Claim 11, wherein the grafting monomer is acrylamide and wherein the graft polymer is subsequently reacted with 1—2 mols of formaldehyde per mol of combined acrylamide.

13. Compositions as claimed in Claim 9 substantially as described and exemplified therein.

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